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Lubrication

A Technical Publication Devoted to the Selection and Use of Lubricants

This Issue

INSTRUMENTAL ANALYSIS OF PETROLEUM

PUBLISHED BY
THE TEXAS COMPANY
TEXACO PETROLEUM PRODUCTS

Lubricating plan cuts downtime —can save $10,000 in 3 hours

Not so long ago, machines shut down by bearing failure could make up production losses. Today volume output and integrated production mean that production losses are losses in profit. These are the reasons behind management's growing concern with lubrication methods in their plants.

Take this example from the paper industry: they used to figure $500 for a bearing, $500 for labor (idle time and repair crew) and expected to make up losses on the two or three hours downtime. Today, high speed machines produce twenty-five tons of paper per hour worth $130 per ton. You can't ignore $3,000 an hour in production losses. In this case, the cost of the bearing replacement could run as high as $10,000.

Lubrication problems differ with specific industries, but the basic principles are the same. Many companies are finding that the services of a plant lubrication engineer pay off. His services can extend part life, eliminate production losses, reduce rejects, simplify lubricant inventories and otherwise add to income. Some companies delegate lubrication responsibility to engineers or plant personnel who also perform other duties.

In both cases, Texaco's organization of Lubrication Engineers is functioning in all 48 States, as consultants in outlining a practical approach to these problems. A more detailed discussion is available in an enlightening booklet: "Management Practices That Control Costs Via Organized Lubrication." Write:

The Texas Company, 135 E. 42nd St., New York 17, N. Y., Dept. L10.

LUBRICATION IS A MAJOR FACTOR IN COST CONTROL

(PARTS, INVENTORY, PRODUCTION, DOWNTIME, MAINTENANCE)

LUBRICATION

A TECHNICAL PUBLICATION DEVOTED TO THE SELECTION AND USE OF LUBRICANTS

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Instrumental Analysis of Petroleum

THE January issues of this publication for the last three years have described analytical techniques used in determining characteristics of petroleum products. The following supplements those previous issues and describes another important phase of petroleum technology, namely, instrumental analysis.

Previously a chemist in the petroleum laboratory spent his time with tedious procedures of wet chemistry and routine test-tube analyses which often required days. Research and development projects were often slowed to a snail's pace. Delays in measuring product quality caused serious loss of production and shipping time. Today's modern instrumentation provides easier and faster methods of analysis.

Though most of the basic principles were discovered prior to 1900 it was not until about 1930 that stable electronic circuits enabled manufacturers to produce many useful analytical instruments. Even then, few instruments as we know them today were available. The present era of really amazing progress in instrumentation was born out of the demands for relatively fast methods for testing huge quantities of materials required for World War II.

This article does not attempt to cover the entire field of analytical instruments used in a modern petroleum laboratory. Rather, it briefly describes four major divisions of instrumentation and relates them to the analysis of petroleum. Three of these, **Absorption, Emission** and **X-ray spectroscopic techniques,** have common ground in that they are concerned with bands of radiation found in the electromagnetic spectrum. The fourth analytical technique considered is **Mass Spectroscopy.**

Spectroscopy is a very broad term and may be simply defined as a study of spectra. It is concerned with the relationship between radiant energy and matter. This radiant energy is electromagnetic in nature and has a particular wavelength as shown in Figure 1 according to the kind of instrument and radiation being employed. The science of spectroscopy dates from the discovery by Newton in 1672 that the amount of refraction undergone when visible radiation or light is passed through a prism, varies with the color of the light to produce a spectrum of primary colors as illustrated in Figure 2.

INFRARED ABSORPTION SPECTROSCOPY

As the name implies, Absorption Spectroscopy is the study of the relative amount of radiant energy of various wavelengths which is absorbed by matter. In order of increasing wavelength each of the following bands of radiation form the most frequently used characteristic groups: Ultraviolet, Visible, Near Infrared and Infrared. Measuring the absorbance or transmittance of such radiations as a function of their wavelength when they pass through liquids or gases, constitutes the science known as Spectrophotometry. Early work in the absorption field was done

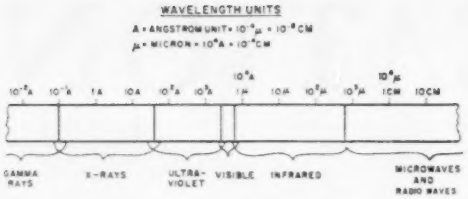


Figure 1 — Electromagnetic spectrum.

in the visible range using the eye to compare depth or degree of color of known and unknown in convenient glass tubes. However, in the past several decades the use of electronics and sensitive photoelectric detectors have made possible very accurate absorption analysis over a much broader range using an instrument known as a spectrophotometer. Figure 3 shows the essential features of this type of instrument. They are: 1) a source of radiation such as visible light, 2) a medium to disperse the radiation such as a prism, 3) a slit to select a narrow band of the radiant energy, 4) a cell to hold the sample, 5) a phototube or other device to detect the radiation coming through the sample at particular wavelengths, 6) electronics to amplify this detected radiant energy and 7) a chart or meter to record or show this amplified energy. For the sake of brevity, this section describes only the details of the Infrared Spectrophotometer; however, principles and techniques would usually apply to the other absorption groups mentioned above.

Ordinary visible light is made up of seven primary colors as shown schematically in Figure 2. The color of an object depends on the wavelength of visible light which it reflects. For example, a white rose reflects *all* wavelengths or colors and a blade of grass absorbs all but the green band which it reflects. Essentially, the same principle is involved in the absorption of infrared rays by organic liquids.

With half a century's progress since Coblentz's initial studies in 1903, we now know that all molecules are made up of atoms connected by chemical bonds which act very much like springs. These atomic groups are in continuous motion with respect to each other, and each molecule has definite vibration frequencies. Two identical molecules have the same atomic pattern and have the same set of vibration frequencies. When radiant energy of the same frequency as one of the natural frequencies of the molecule hits the molecule it is excited into sympathetic vibration. This exchange of energy from the radiation to the molecule causes the radiation to be weakened and absorbed. It also produces changes in the vibrational and rotational energy of the molecule. In one sense the infrared spectrum is an analysis of molecular vibrations.

All organic molecules are capable of absorbing energy at some spectral position in the infrared region and a very valuable characteristic of infrared is its specificity. The infrared spectrum is the most nearly unique property of a substance since even isomers which have the same number and kind of atoms but different geometrical arrangement are readily differentiated. These isomers which often vary markedly in chemical activity are very difficult to distinguish by other analytical methods.

Modern infrared spectrophotometers, such as that pictured in Figure 4 and schematically illustrated in Figure 5, are designed and built on the double beam optical null principle. The infrared energy is split into two beams of equal intensity near the source, which is either a hot carborundum rod or a Nernst glower. One beam passes through the sample cell and is known as the sample beam, the other beam passes through the reference cell and is called the reference beam. A calibrated optical wedge or comb is located in the reference beam and moves in and out mechanically so as to block off radiation in the reference beam equal to the radiation the sample is absorbing from the sample beam. The movement of the optical wedge to maintain the null position is connected mechanically with the chart pen and gives a continuous record of the transmittance of the sample. The sample and reference beam systems give rise to the term "double beam" while the mechanical balancing of the two beams result in the term "optical null".

The double beam principle offers several advantages for analytical applications. First, the I_o curve, that is, the transmittance curve obtained with no sample in the instrument, is a flat, straight line at or near 100 per cent transmittance from 2 to 16 microns. Thus, no mathematical correction is necessary because of non-linear I_o radiation. Second, atmospheric absorption due to water vapor and carbon dioxide, often a cause of troublesome interference, is compensated out of the spectrograms by the double beam operation. Third, the double beam principle permits the convenient use of solvents in qualitative and quantitative analysis. By the use of

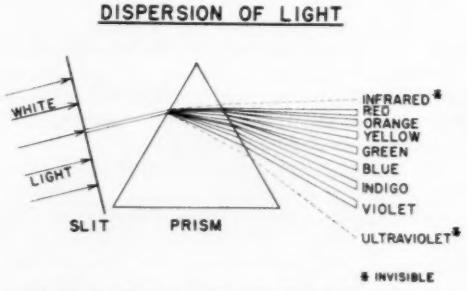


Figure 2 — Refraction of white light with a prism.

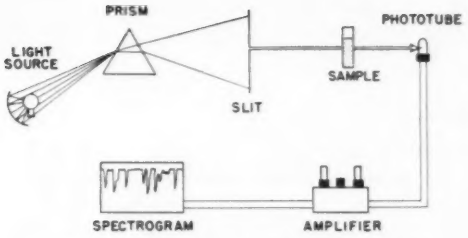


Figure 3 — Diagram of a spectrophotometer.

carefully matched sample cells, any absorption due to solvents is compensated out of the spectrograms leaving only the spectra of the sample on the chart. Finally, the double beam principle permits the use of differential analysis. In this technique, similar samples are placed in matched cells. Absorption common to both samples is compensated out, and only differences between the two, due to the substance being determined, appears on the record. This technique is quite sensitive, and often detects traces of substances which otherwise could not be found. While not directly related to basic design, the modern infrared spectrophotometer incorporates a number of desirable features for convenience of control and operation. Some of these are: (1) manual and automatic slit programming, (2) wide choice of scanning speeds, and (3) the ability to expand a small selected portion of the infrared region for detailed examination.

Qualitative Application

The spectrum of an unknown sample gives useful information about its molecular structure. Organic compounds contain various combinations of atomic building blocks, also referred to as functional groups such as O-H (*hydroxyl* as in ethyl alcohol), and

Figure 4 — Infrared spectrophotometer.

C=O (*carbonyl* as in acetone). The dashes in these blocks indicate interatomic bonds. A building block always has the same atomic pattern and gives characteristic bands regardless of the structure of the rest of the compound. Thus an infrared spectrum consists of characteristic absorption bands of these functional groups as well as bands characteristic of how these building blocks are put together. Inspection of an unknown spectrum such as that of gasoline illustrated in Figure 6 shows immediately which blocks are present. In qualitative analysis the building blocks are the keys to the identification of the unknown as a search is made in a library of known spectra.

Since an infrared spectrum is a fingerprint of that material, the matching of the infrared spectrum of an unknown sample with that of a known sample is accepted as proof of identity. With an extensive library of pure spectra, the identification of a single component is a relatively simple sorting procedure. However, most samples are complicated mixtures of liquids and solids requiring detailed study and care-

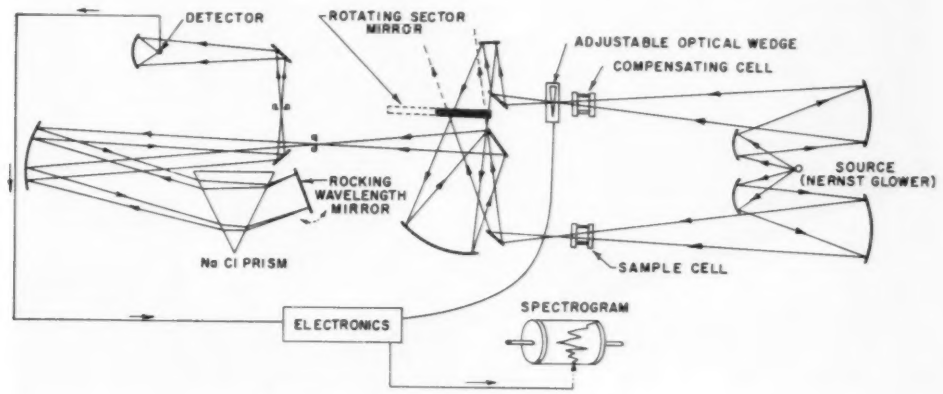


Figure 5 — Diagram of an infrared spectrophotometer.

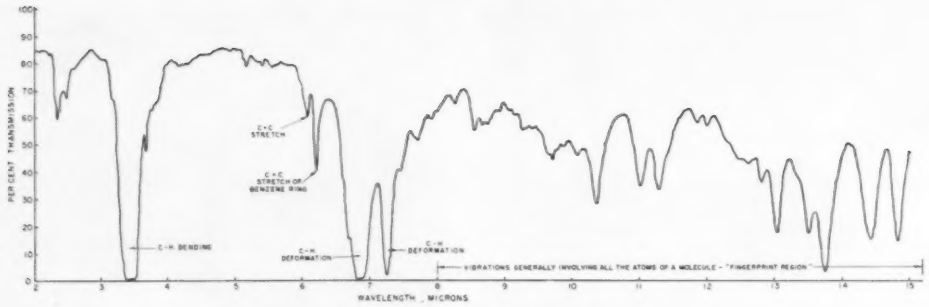


Figure 6 — Typical infrared spectrogram of a gasoline.

ful interpretation of the spectra. Although the infrared spectrum does not, as if by magic, show formulae of unknown mixtures, yet its clues when carefully evaluated save many days in the time required for a complete analysis.

An advantage of absorption analysis is its rapidity; many complete analyses are performed in 15 minutes. Samples are recovered in unchanged condition after an analysis and there is a permanent record of each analysis that can be used for future reference and comparison. Only a small amount of sample is needed for an analysis — at times a few milligrams is sufficient.

Quantitative Application

Quantitative analysis is based on the fact that a substance absorbs a particular wavelength of infrared radiation in proportion to its concentration.

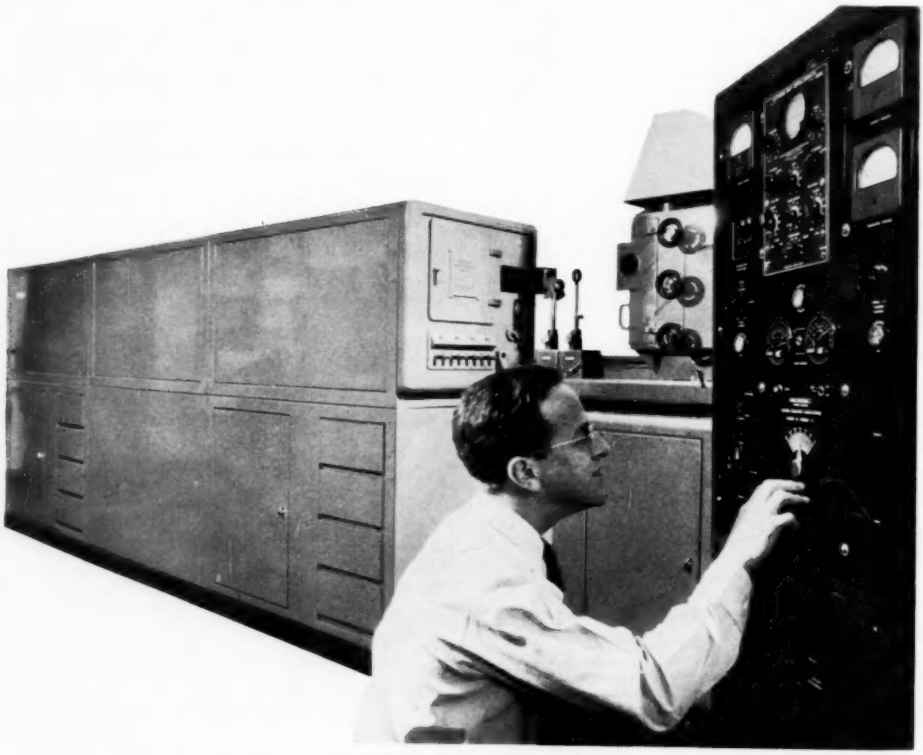


Figure 7 — Emission spectrograph.

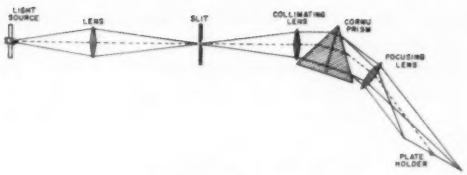


Figure 8 — Diagram of a prism spectrograph.

Comparing the absorption of a sample with that produced by known amounts of a standard sample gives the concentration of the unknown. This type of analysis is often carried out on additive materials in lubricants. Infrared is used to advantage to follow changes which occur during the life of a lubricant. Typical changes which may be followed are: depletion and degradation of additives in oils and greases, oxidation of oils, and contamination of lubricants with extraneous materials. In petroleum processing, infrared is used to continuously measure isobutane in alkylation units. It is a very convenient tool in automotive research for following the reactions in combustion cylinders and for the continuous analysis of exhaust gases.

Many are the interesting applications of infrared outside the petroleum industry. Infrared methods are challenging radar in reconnaisance, warning and fire control. Even a three-inch scanner can distinguish the engines on a single plane at a distance of five miles. In medical research infrared was the basic tool in determining the structure of penicillin and in guiding the synthesis of cortisone. Railroad people are detecting hot boxes in the cars by an infrared device placed in the roadbed.

EMISSION SPECTROSCOPY

Though known for over 100 years the principles of emission spectroscopy have only been applied to analytical problems in the petroleum industry for the last 25 years. This rapid and accurate method of analysis awaited the arrival of good quality instrumentation. Emission spectroscopic analysis is based on the fact that atoms of most elements when brought to an incandescent or excited state emit radiation of various wavelengths which are characteristic of that element. An electric arc or spark is generally used to excite the atoms. This radiation is then sorted by an instrument called a spectrograph, pictured in Figure 7, which uses a prism or a diffraction grating as the actual wavelength "sorter". A photographic plate or photoelectric cell detects the radiation of various wavelengths entering the spectrograph through a narrow slit. When a photographic plate is used the result is a series of short vertical lines, which are actually images of the slit as shown in Figure 9. Actually there are many more lines — only some of the stronger ones are shown.

Two basic types of spectrographs are the prism (diagrammed in Figure 8) and the grating, each named after its optical medium employed to disperse the radiation. Spectrochemical analysis can be performed satisfactorily with both types and choice of instrument depends on several factors such as cost, space, and the type of samples to be analyzed.

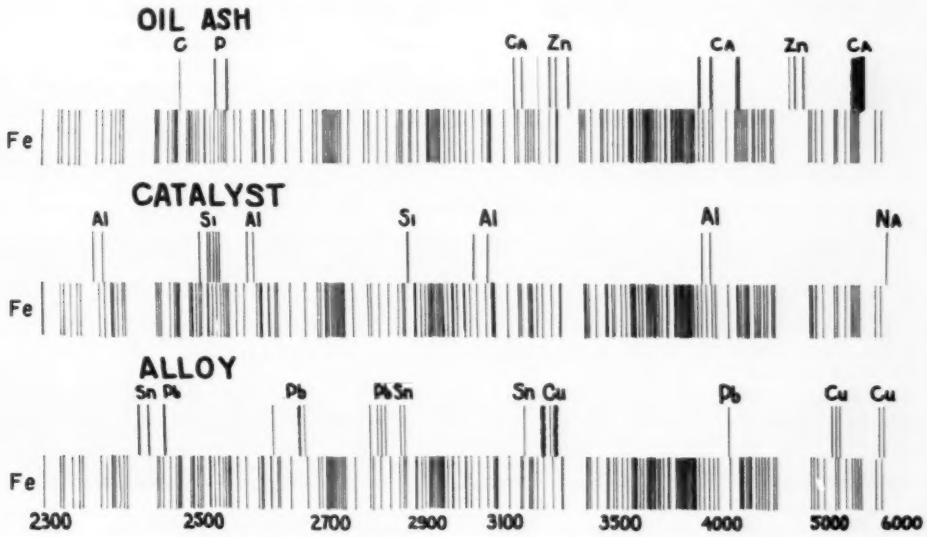


Figure 9 — Three idealized emission spectra with iron reference spectra.

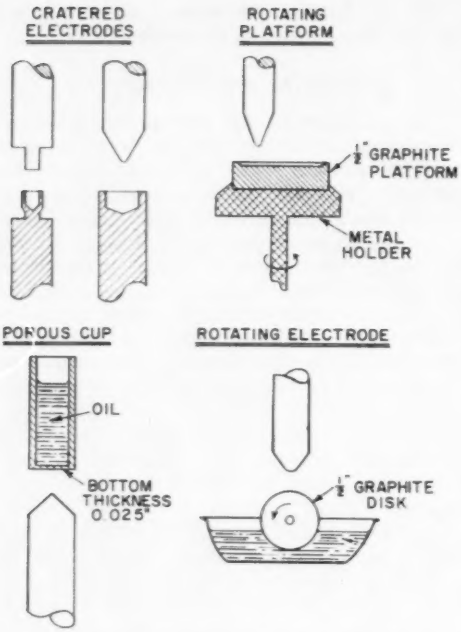


Figure 10 — Four spectrographic electrode systems.

Prism instruments have good dispersion and resolution in the ultraviolet region where lines of greatest analytical significance lie. Prisms are usually made of quartz with angles of either 30° or 60° depending on their mounting in the spectrograph.

Spectrographic gratings are usually concave mirrors ruled with 15,000 to 30,000 lines per inch. Grating spectrographs have higher dispersion and greater resolution at longer wavelengths, resulting in greater distances between lines. Greater dispersion is necessary when working with very complex spectra having a large number of lines.

Five common electrical sources for supplying thermal energy for sample excitation are: high voltage AC spark, high voltage AC arc, low voltage AC arc, DC arc, and the unidirectional DC arc. Of these, the DC arc is the most suitable for general *qualitative* analysis because of its high thermal energy and high sensitivity. All five sources are used for *quantitative* work, the choice depending mainly on the type of sample being analyzed and the technique employed.

Qualitative Analysis

To determine what elements are in a sample, the processed photographic plate is viewed by transmitted light on an opal glass reader with a magnifier. Just below each sample spectrum an iron spectrum is recorded as illustrated in Figure 9. The iron spectrum is obtained by arcing two very pure iron rods and serves as a guide and reference scale to aid in the qualitative interpretation of other spectra. An analyst becomes familiar with the main lines of each element with respect to the lines of the iron spectrum as illustrated in the three idealized spectra of Figure 9. The figures appearing beneath the lowermost spectrum give the radiation wavelengths in Angstrom units. The analyst usually has standard spectra of each of the elements of interest along with the iron spectrum for ready reference and comparison. In case of unusual and complex samples he may refer to published spectra charts and wavelength tables. There is no substitute for experience in the interpretation of spectra, which is one of the most difficult jobs in a spectrographic laboratory.

Since the number of spectral lines and their intensities are proportional to the concentration of the elements, qualitative emission spectroscopy can also be used as a fast method for estimation of sample composition. However, before an element can be classified as "major", "minor", or "trace", many factors must be considered including the type of sample, the weight of the original sample, the weight of material arced, the effect of the base material on the spectrum of each element, the relative volatility of the molecular form of each element, and, if it is available, the history of the sample. This technique is applied to the *qualitative* detection of innumerable materials such as metals and some non-metals in new and used oils, greases, catalysts, minerals, deposits, alloys, gasolines and crude oils.

Quantitative Analysis

Quantitative spectrographic analysis is conducted on an empirical basis with known standards similar in composition to the unknown sample being run under as nearly identical conditions as possible. The per cent transmittance of each element line of interest is measured by an instrument called a densitometer and converted to an equivalent function called the "relative intensity". This is used to determine concentration by means of one or more analytical curves for each element.

The preparation of samples for excitation in quantitative analysis is one of the most critical steps.

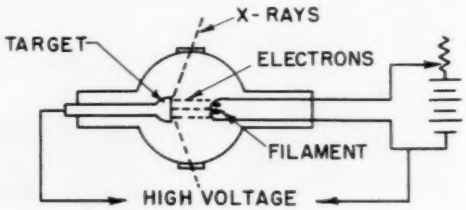


Figure 11 — Diagram of x-ray source.

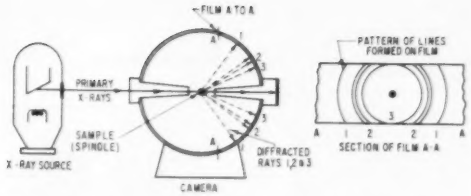
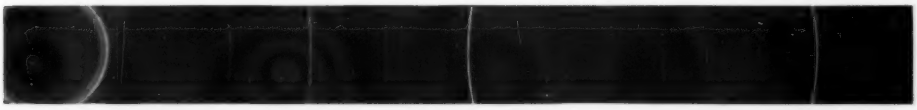


Figure 12 — Diagram of x-ray film diffraction technique.

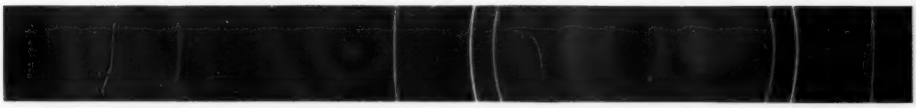
Organic liquids are analyzed by direct or indirect methods using one of the four electrode systems illustrated in Figure 10. In direct analysis the liquid itself enters the arc or spark column. With indirect techniques the metallic elements in the sample are first concentrated by coking or ashing. This residue is packed into a cratered electrode and subjected to a DC arc. Another technique makes use of a revolving horizontal graphite platform on which a few drops of the liquid sample have been vaporized.

The densitometer measures the darkness or density of any particular line in a spectrum for quantitative analysis. Light from a lamp filament is concentrated on the spectrum line on the photographic plate and that which passes through the line is then focused by a suitable optical system onto a photoelectric cell. The electrical output from this cell is amplified electronically and measured by a galvanometer. The amount of light passing through the line is compared with the amount that passes through a clear, unexposed portion of the photographic plate or film. By this means, the per cent transmittance of the line is obtained.

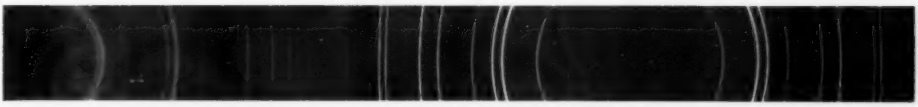
In quantitative emission analysis one encounters variables such as wandering of the arc, variations in the electronics of the source unit, and difference in photographic emulsions which are difficult to control. These variations are effectively minimized by adding to both the sample and the standard equal amounts of a material called an "internal standard." Intensity of an element line is divided by the intensity of the internal standard line to give an "intensity ratio." Such ratios from several concentrations of known standards are then used to plot the analytical curve. Concentration of the unknown is then obtained by referring its intensity ratio to the ana-



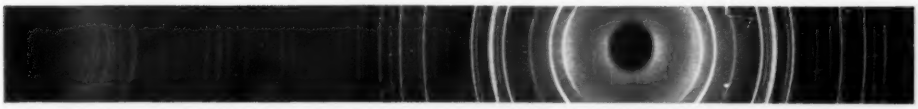
a. Pure metallic iron.



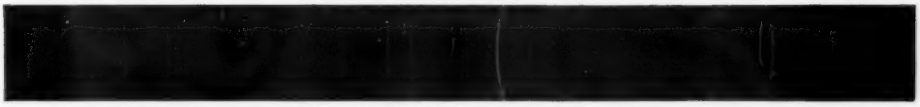
b. Ferrous oxide (FeO).



c. Alpha ferric oxide (Fe_2O_3).



d. Hydrated ferric oxide ($Fe_2O_3 \cdot H_2O$).



e. Magnetic iron oxide (Fe_3O_4).

Figure 13 — X-ray diffraction patterns of iron and four common oxides.

TABLE I

Successive spectrographic analyses of used oil from a diesel locomotive crankcase

Sample No.	1	2	3	4	5	6	7
Engine Miles	501000	509000	516000	533000	538000	547000	554000
Miles Since Last Oil Change	4000	12000	19000	36000	4000	13000	20000
Iron (Fe) ppm.	17	18	20	39	12	19	23
Lead (Pb) ppm.	21	24	31	59	11	17	24
Copper (Cu) ppm.	14	16	17	36	12	16	21
Chromium (Cr) ppm.	1.0	1.8	2.0	51	4.3	2.9	1.4
Silver (Ag) ppm.	0.32	0.43	0.54	2.1	0.27	0.38	0.51

lytical curve. The principle is that variations during the analysis affecting the line intensity of the element being determined will have approximately the same effect on the internal standard line so that the intensity ratios will remain essentially constant and will give a reliable index of concentration.

Direct reading spectrographs which give greater accuracy and speed are now available from several sources. Such instruments give analytical results directly using photomultiplier tubes to measure the intensity of the lines of the spectra. The instruments have high sensitivity, relatively good precision and are several times as rapid as the photographic plate-densitometer equipment. They are capable of measuring concentrations ranging from major constituents down to trace components as little as one tenth part per million.

Emission spectrochemical analysis is a versatile tool for solving a variety of problems. Because it uniquely combines both speed and accuracy, it is widely used in the petroleum and other industries for research and development, manufacturing and maintenance control. The emission spectrograph has an interesting use in refinery operations for analysis of crude oils for trace metals such as iron, vanadium and nickel. Since these metals influence product yield in catalytic refining it is important to know their concentration in the crude oils, catalytic charge stocks and in the catalysts. The spectrograph is also used for the analysis of residual fuel oils in which natural traces of metallic elements are concentrated during the distillation processes. When used as a fuel in high temperature boilers and turbines, excessive quantities of elements such as vanadium may cause troublesome deposits, slag and pitting.

Spectrochemical analysis is extensively used as a maintenance tool for diesel locomotives. Its application is to warn of impending failure of an engine due to excessive wear or corrosion of vulnerable parts which is usually evidenced in the oil as a sudden and rapid rise in such trace elements as iron, copper, lead and silver. A potential failure is illustrated in Table I. Samplings 1 through 3 indicate gradual and normal increases in iron, lead, copper and silver, the metals usually associated with wear and corrosion. Sample #4 shows abrupt increases in these elements along with a large rise in chromium content indicating a serious water leak from the cooling system where chromium salts were used as corrosion inhibitors. After this sampling the oil was drained, the engine inspected and repaired, and the locomotive returned to satisfactory operation.

The emission spectrograph also insures another aspect of maintenance in that it conveniently measures depletion of metallo-organic additives in used lubricating oils and thereby helps to establish optimum drain intervals.

Spectrographic methods are valuable as a guide and aid in other types of analyses. In many instances they are used to reduce the number of steps in chemical quantitative work, to check the purity of a precipitate and to determine the completeness of a chemical separation.

X-RAY

Another analytical tool makes use of x-rays as the source of radiant energy. Note from Figure 1 that x-rays are also part of the electromagnetic spec-

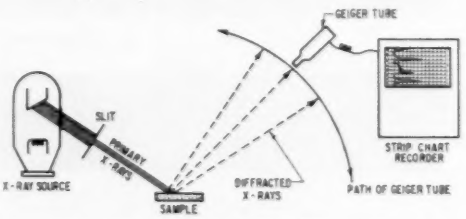


Figure 14 — Diagram of x-ray diffractometer.

Figure 15 – X-ray diffractometer with electron circuit panel.

trum and are of short wavelength, of the order of 0.1 to 100 Angstrom units. They were discovered in 1895 by Roentgen and may be produced by bombarding a metallic target with high speed electrons. Figure 11 illustrates how electrons are emitted from the hot filament in the vacuum tube and are attracted to the target material which is positively charged to a potential of 15 to 50 thousand volts. When these electrons hit the target, x-rays are produced with wavelengths characteristic of the target material. Moseley had shown that the wavelength of the x-rays bore a direct relationshp to the atomic number of the target material and also that they are roughly of the same magnitude as the interatomic distances in crystalline material.

A crystal is an orderly arrangement of atoms in a sort of three-dimensional lattice. Such a periodic arrangement has planes in which the atoms are more abundant than in other planes and all these planes may be inclined at various angles. X-ray diffraction does not analyze the geometric relations of the faces of the crystals but rather the periodic arrangements of the atoms within a crystal and the distances between these planes.

If x-rays of known wavelength are diffracted by a crystal, one can determine the distance between the atomic layers of the crystal, thereby obtaining a "fingerprint" of its identity merely by measuring the angles at which the x-rays are diffracted. Conversely, the wavelength of the x-rays may be calculated if a crystal of known spacing is used to diffract the rays. This principle is the basis for both x-ray diffraction and x-ray fluorescence analytical methods. Present-day instrumentation has utilized these facts and others to develop accurate methods for qualitative and quantitative analyses. Following are descriptions of the three most widely used types of x-ray analytical techniques.

X-Ray Film Diffraction

In this technique which is illustrated schematically in Figure 12, the x-ray beam enters the camera and is diffracted by the unknown sample onto a photographic film which records a "diffraction pattern" as a series of circular lines or bands that are characteristic of the substance or substances in the sample. Figure 13 presents five such diffraction patterns of metallic iron and its several oxides.

If the unknown sample under investigation is amorphous (non-crystalline) like some glass, rubber, or water, the x-ray diffraction pattern will show no lines but merely a wide band or shadowing effect. When the unknown material is crystalline, however, the lines are sharp and the more crystalline the substance, the sharper the lines will be.

Unknown materials are likely to contain many component substances. If attempt were made to analyze the unknown in its "as received" condition, the x-ray beam could conceivably concentrate on one or a very few of the component substances and ignore the remainder. Therefore to insure a truly representative x-ray diffraction pattern, an unknown material is reduced to a fine thoroughly-mixed powder, formed with adhesive into a small cylindrical spindle and finally rotated at the center of the camera during exposure to the x-ray beam.

An ASTM card catalogue is available which contains data on the position and intensity of x-ray diffraction lines for thousands of pure crystalline materials of known composition. These along with additional patterns that have been obtained in many special fields of work permit identification of crystalline unknowns by comparison of patterns.

It is important to note that x-ray diffraction patterns on crystalline materials give an analysis of the compounds present as well as their component elements. To emphasize this important characteristic, attention is again invited to Figure 13 which illustrates the easily discernable differences in x-ray diffraction patterns among pure iron and four of its more common oxides. Ordinary "wet" chemical analysis of a mixture of these oxides would give only the total amounts of iron and oxygen present but without indication of *how* they were combined.

As a further example, titanium oxide (TiO_2)

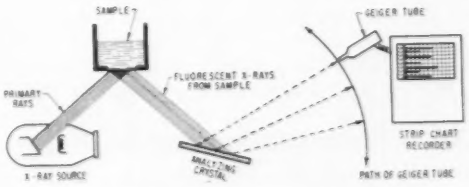


Figure 16 – Diagram of x-ray fluorescent spectrograph.

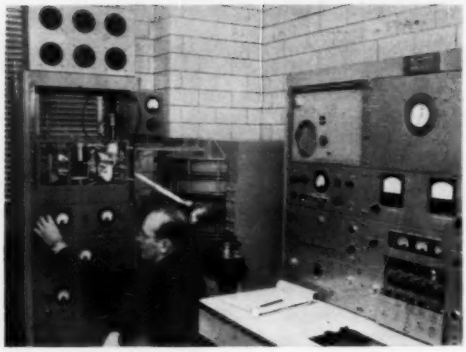


Figure 17 — High temperature mass spectrometer for analysis of high molecular weight materials.

exists in the three allotropic forms of rutile, anatase and brookite. Since all three contain the same amounts of titanium and oxygen, purely chemical analyses would not distinguish them, but their x-ray diffraction patterns are so vastly different that instant identification can be made.

In the petroleum industry, x-ray diffraction is widely used for the qualitative analyses of such materials as sludges, catalysts, deposits, stains, alloys, minerals and corrosion products. This method is particularly advantageous since an analysis can be obtained on a sample as small as the period at the end of this sentence. And since the sample is not destroyed, it can be recovered for further tests.

X-Ray Diffractometer

As shown schematically in Figure 14 and pictorially in Figure 15, this technique is similar in principle to the preceding except that a Geiger tube and strip chart are used in place of photographic film to measure and record the data. When adequate sample is available, this method is more rapid than the preceding for qualitative analysis. It is also a very convenient and rapid method for quantitative analysis, since the heights of the peaks on the strip chart are directly proportional to the concentration of the corresponding compound. Peak location tells *what* is present, peak height tells *how much*.

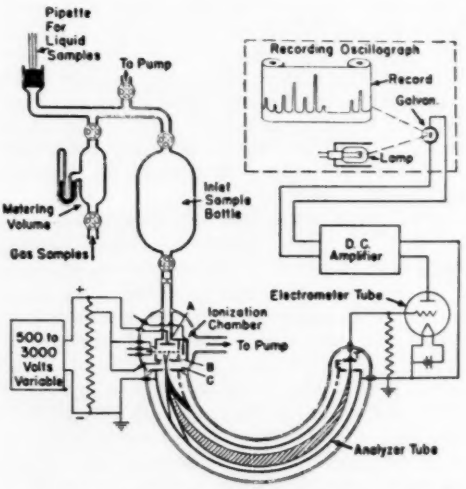
The more highly crystalline a material is, the easier its determination. For example, as little as one percent of the very crystalline alpha Al_2O_3 (aluminum oxide) may be accurately determined in a catalyst that is essentially gamma Al_2O_3 (another similar but less crystalline aluminum oxide).

X-Ray Fluorescent Spectrograph

In this technique as illustrated in Figure 16, primary x-rays hit the sample causing secondary fluorescent x-rays to be emitted. These secondary rays are diffracted by the analyzing crystal and their wavelengths measured. These measurements identify the elements since each element emits its own characteristic wavelengths. In a complex sample, *all* elements present contribute their spectra and differentiation is accomplished by utilizing an analyzing crystal with a known atomic layer spacing which acts as a diffraction grating. As this crystal is rotated, various wavelengths representing individual elements are diffracted, their intensities measured by the Geiger tube and registered on the chart.

This technique also provides an accurate and rapid means of quantitative analysis since the intensity of the fluorescent radiation corresponding to each element is directly proportional to its concentration. Although present instrumentation restricts analysis to elements with atomic numbers higher than 11 it is employed for a wide variety of samples. For example, it is used for the quantitative determination of the metallic components of catalysts, tetraethyllead in gasoline, metals in additives and additive oils, small quantities of metallic impurities in oils, catalysts and charge stocks. This method is direct, accurate to within $\pm 2\%$ of the amount present, and rapid. Determining an additive metal such as barium, calcium or zinc in a lubricating oil or tetraethyllead in a gasoline takes only about 10 minutes per element.

Using the three x-ray techniques, many different types of samples may be analyzed to give important information more rapidly than by classical methods and in many cases not obtainable any other way.



Courtesy of Consolidated Electrodynamics Corporation

Figure 18 — Diagram of a mass spectrometer.

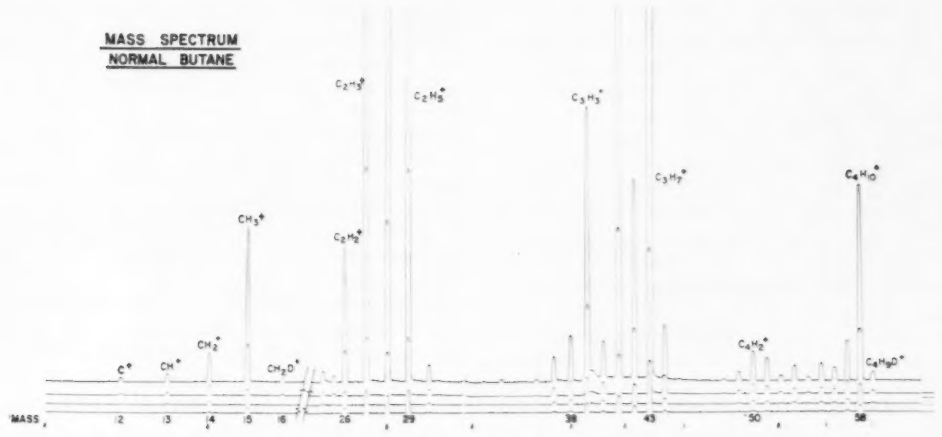


Figure 19 — Mass spectrum of normal butane.

MASS SPECTROSCOPY

Mass Spectroscopy was first introduced as an analytical tool in a petroleum laboratory in 1942. In the beginning it was used primarily for gas analysis, and in that role played a very important part in the Allied aviation fuel and synthetic rubber programs during World War II. A mass spectroscopic method was developed that most opportunely reduced to minutes and hours instead of hours and days, the time required to analyze diverse complex mixtures of fixed gases and light hydrocarbons. Such mixtures are very important in several manufacturing processes of the petroleum and petrochemical industries; they are obtained as by-products in some and are used as feed stocks in other processes.

From the first industrial use 16 years ago when simple gaseous hydrocarbon mixtures were successfully analyzed, the mass spectrometer has been applied to progressively heavier materials and has become one of the most useful laboratory tools for the qualitative and quantitative analysis of hydrocarbons. Although a sample must be in the gaseous state to be suitable for examination, materials as heavy as lube oil distillate may be analyzed with an instrument shown in Figure 17 which can operate at high temperatures and at low pressures where these heavy distillates vaporize into the gaseous state.

The mass spectrometer shown schematically in Figure 18 may be used for the analysis of gases and volatile liquids. A portion of the sample consisting of about 0.2 ml of gas at normal temperature and pressure or 0.001 ml of liquid, is completely vaporized into the evacuated inlet sample bottle, in which the pressure after introduction is about 50 microns of mercury. Then, by opening the valve immediately ahead of the orifice, the molecules are allowed to effuse through the orifice and flow through the ionization chamber toward the high-speed vacuum pump. In the ionization chamber the electrically neutral molecules must run the gauntlet of a stream of bombarding electrons being emitted from the tungsten filament. A statistically small percentage of them are so excited by near misses that they eject one of their own electrons. Other molecules absorb enough of a bombarding electron's kinetic energy from a very near miss or a direct collision that the molecules break into pieces of diverse sizes, weights and shapes. A percentage of the molecular fragments end up deficient one electron. Loss of more than

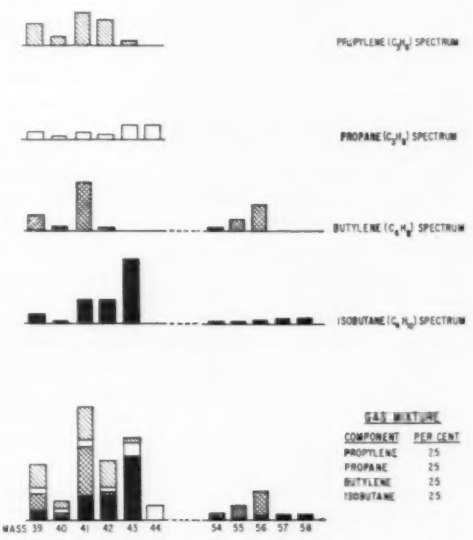


Figure 20 — Graphic illustration of individual and total mass spectra of a four-component gas mixture.

one electron occurs occasionally, but rarely.

The whole molecules and parts of molecules that lost electrons are no longer electrically neutral but are now positive ions. Therefore, the positive potential on the repeller lens (A) pushes them toward the slit in plate (B) where they encounter a strong electrostatic field between plates (B) and (C). This accelerates them out of the ionization chamber into the analyzer tube in a very narrow collimated beam.

The beam of ions, flying in a straight line at speeds up to one tenth that of light, runs into a uniform magnetic field perpendicular to the plane of flight. This causes the ions to travel circular paths, the radii of which are dependent upon the individual masses. All ions of the same mass follow paths of the same radii. Heavy ions are deflected less strongly than the light ones.

By gradually varying the electrostatic field, ion beams of successively greater mass are focused in turn on the exit slit (E), behind which is located the target (T). The electric current imparted to the target electrode (T) is proportional to the concentration of ions of the corresponding mass in the ionization chamber. This current is amplified and fed into a recorder which produces a series of peaks as each ion beam of successively greater mass is focused on the target. The horizontal axis is proportional to the continuously varied electrostatic field, which in turn identifies the ion mass. The vertical axis is proportional to the ion concentration. The graph is called a mass spectrum and that for normal butane (C_4H_{10}) is shown in Figure 19. In the particular instrument used to obtain Figure 19, peaks are recorded simultaneously by four galvanometers at four sensitivity levels, hence four traces are shown.

The relative abundance of ions of different masses formed by electron bombardment of any particular substance depends on the relative probability of the different ionization processes. These in turn are related to molecular structure, including spacial configurations. Consequently, under constant conditions of ionization, each particular substance is identified by a particular mass spectrum, which is a fingerprint of that substance.

The mass spectrum of a mixture of substances is the summation of the individual mass spectra of the components as shown in Figure 20. Using modern high-speed computing equipment, the mass spectrum of a mixture of fixed gases and hydrocarbons with up to 6 carbon atoms containing more than 20 individual components can be unraveled and the quantitative analysis obtained in a matter of only a few minutes.

Individual component analyses of hydrocarbon samples is feasible for the most part through about the C_7 region (molecules containing seven carbon atoms). Straight-chain paraffins (C_nH_{2n+2}) when present essentially alone, as in petroleum wax, or when separated from other hydrocarbons by chemical or physical techniques may be determined individually up to about C_{50}. Olefins (C_nH_{2n}) containing more than four carbon atoms introduce difficulties because of the great number of possible isomers. However olefins may be removed from the sample by physical separation methods then hydrogenated and determined as the corresponding paraffins. While this expedient gives the geometrical configurations of the former olefins it does not reveal the number and position of their double bonds. Paraffins containing up to nine carbon atoms can be determined individually except for a few pairs of isomers which must be analyzed as a group.

Much of the preceding discussion concerned the dissimilarity in mass spectra between different compounds and isomers. However, there also exists certain similarities in mass spectra between compounds of any one type, i.e., paraffins, olefins, naphthenes, alkyl benzenes, indans, naphthylenes, anthracenes, etc. All the compounds in any one type display in their mass spectra quantitative characteristics of fragment distribution which under certain conditions, identify that type. This is the basis of mass spectroscopic analysis of high molecular weight materials in the kerosene and heavier distillate region.

Obviously, the simpler the mixture of hydrocarbons present, the simpler is the job of analysis. Most hydrocarbon mixtures in the heavier distillate range must first be subjected to methods of separation such as distillation and chromatographic techniques if maximum information is to be obtained. The interpretation of the spectra is usually extremely difficult and in many cases the results are only of a semiquantitative nature. Nevertheless a small number of high molecular weight mass spectrometers are being used in research laboratories to correlate hydrocarbon composition with variations in oil properties and processing methods.

SUMMARY

Although the four instrumental techniques described herein represent only a part of the field, they do serve to illustrate the principles and applications of instrumental analysis to petroleum. From an economic standpoint a recent survey revealed that the majority of analytical instruments save enough in man-hours to pay for themselves in less than two years. In addition they give important information which in many cases would be impractical to obtain by other means. In short, instrumental analysis provides an efficient solution to a variety of analytical problems whether they originate from research, production, application or any one of the thousand areas where fuels and lubricants are used.

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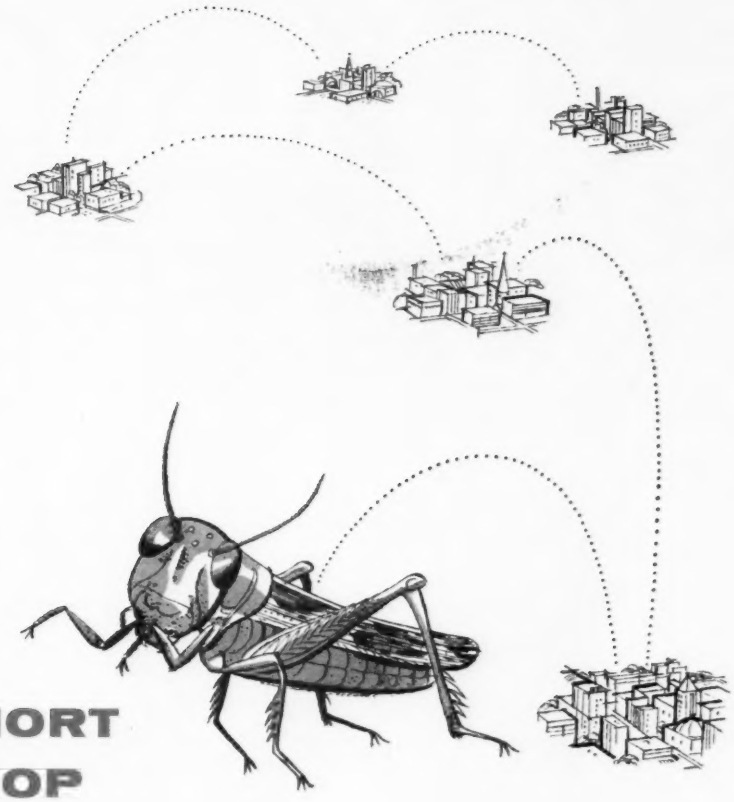

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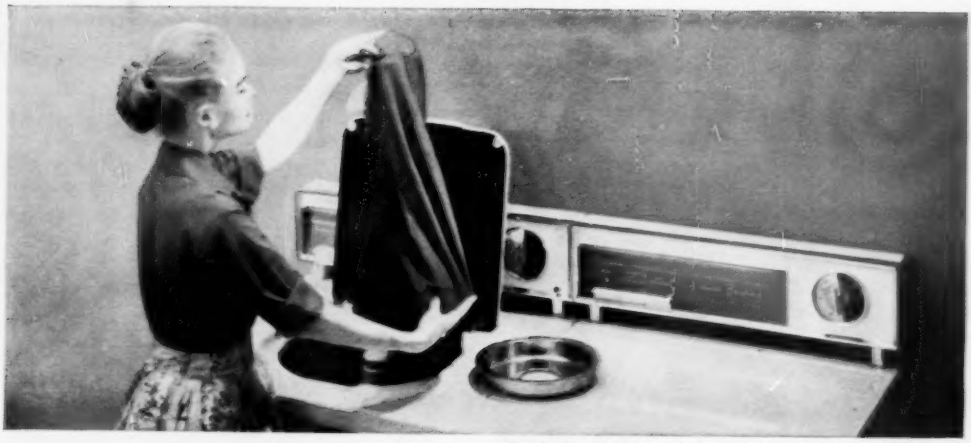

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